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The effect of aqueous alcohols (methanol, *t*-butanol) and sulfolane on the dissociation constants and thermodynamic properties of alkanolamines

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ABSTRACT

The dissociation constants of protonated monoethanolamine, N-methyldiethanolamine have been determined in aqueous mixtures of methanol, *t*-butanol–water and sulfolane solvents. The mole fractions of the organic compounds ranged from (0.2 to 0.95) and the temperatures from (283 to 353) K. Standard state thermodynamic properties like $\Delta_r G$, were derived from the results. The basic strength of the protonated alkanolamine decreased with decreasing dielectric constant and increase in temperature of the solvent.

1. Introduction

Alkanolamines are used for the removal of acid gases such as CO_2 and H_2S from industrial and natural gas streams. The dissociation constant is one of the important properties in the selection of an (alkanol)amine solution for acid gas removal or in the interpretation of the kinetic mechanism of the reactive absorption of the acid gas into the (alkanol)amine solution [1].

A typical acid gas removal plant is operated with an acid gas absorption/desorption cycle of the acid gas [1]. In the absorber, the acid gas is (chemically) absorbed by the solvent. By operating the stripper at a higher temperature and in the case of natural gas sweetening also at near atmospheric pressure, the basic strength of the solvent is reduced and the acid gas is released. The basic strength is reduced as a result of lower dissociation of the unprotonated solvent at higher temperatures [2,3]. The same behavior of lower dissociation (and basic strength) may also be achieved by reducing the value of the dielectric constant of the solvent by the addition of an organic compound. The basic strength of the solvent is thus reduced without any increase of the temperature, yet enhancement of temperature will lead to further fall in basicity. By adding an organic compound, the acid gas may be released from the solvent at lower temperatures.

The organic compound can be

(1) an alcohol. The alcohol may be added to the incoming acid gas loaded solvent at the onset of the desorption process in the stripper, and removed together with the acid gas by evaporation before the lean solvent is directed back to the absorber. The alcohol and the acid gas can readily be separated, and the alcohol returned to the desorber. Hence, an alcohol cycle is added to the conventional absorption/desorption cycle in terms of a distillation
(2) another organic compound frequently used in acid gas treating processes, e.g. sulfolane. These types of organic compounds can be added as a part of the solvent circulating through the absorber and the desorber, and should lead to overall favorable effects of the acid gas removal process, e.g., by reducing the stripping ratio and consequently a reduction in reboiler duty.

Recently, Barzagli et al. have conducted the CO_2 absorption and desorption experiments with alkanolamine blends in non aqueous solvents (mixtures of ethylene glycol and 1,2-propandiol with methanol or ethanol) [4]. They have reported relatively low stripping temperatures (as low as 80 °C) and reduced evaporation and have shown that the amine regeneration is easy in non-aqueous solvents (Fig. 1).

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a	activity of component i
B	second virial coefficient in Pitzer's equation
b	constant in the modified Debye–Hückel term/kg$^{1/2}$ mol$^{-1/2}$
b'	empiric parameter used for radius estimation
C	third virial coefficient in Pitzer's equation
C_P	heat capacity/J (mol K)$^{-1}$
E	electromotive force/mV
e	charge of electron/C
E°	standard potential/mV
F	Faradays constant/C mol^{-1}
f	modified Debye–Hückel term
G	specific Gibbs energy/kJ mol^{-1}
H	enthalpy/kJ mol^{-1}
K	dissociation constant
k	Boltzmann constant/J K^{-1}
K_{ap}	solvent autoprotolysis constant
M^*	mean relative molar mass/g mol^{-1}
n	number of moles
N_A	Avogadro constant/mol^{-1}
p	pressure
R	gas constant/J (mol K)$^{-1}$
r	ion radius/Å
S	entropy/J (mol K)$^{-1}$
T	temperature / K
x	mole fraction
A_ϕ	Debye–Hückel parameter/kg$^{1/2}$ mol$^{-1/2}$
$\overline{m}_i$	overall molality of component i/mol kg^{-1}
$\tilde{m}$	total mass/g
$\tilde{M}$	molar mass of pure component/g mol^{-1}
$\overline{n}_i$	overall number of moles of component i/mol
$\tilde{n}$	total number of moles/mole

Greek letters

α	constant in Pitzer's equation/kg$^{1/2}$ mol$^{-1/2}$
$\beta^{(0)}$	binary interaction parameter in Pitzer's equation/kg mol^{-1}
$\beta^{(1)}$	binary interaction parameter in Pitzer's equation/kg mol^{-1}
Δ	difference
ϵ	relative dielectric constant of the solvent
ϵ_0	permittivity of a vacuum/C^2 N^{-1} m^{-2}
γ	activity coefficient
μ	chemical potential/J mol^{-1}
ρ	specific density of the solvent/kg m^{-3}

Superscripts

$^\circ$	standard state
$^\otimes$	standard state on molality scale
ex	excess

Subscripts

a	acid
b	base
C	critical
I, II	cell (I), cell (II)
m	molar, on molality scale
r	reaction
c	on molarity scale
i, j, k	ionic component *i, j, k*

Abbreviations

Alc	alcohol
aq	in aqueous solution
elec.	electrostatic
exptl	experimental
MDEA	N-methyldiethanolamine
MeOH	methanol
non.	nonelectrostatic
Sulf	sulfolane
SH	fictitious amphoteric solvent
s	solid
TBA	*t*-butanol
TEA	triethanolamine
W	water

The dissociation constants of protonated monoethanolamine (MEA), N-methyldiethanolamine (MDEA) have been measured in *t*-butanol–water (TBA), sulfolane–water and protonated triethanolamine (TEA) has been measured in methanol. The fractions of the organic compounds were ranging from 0.2 to 0.95 and the temperatures from 283 to 353 K.

2. Procedure

In an aqueous organic solvent, a protonated (alkanol)amine dissociates according to:

$$R - NH_3^+ + SH \rightleftharpoons R - NH_2 + SH_2^+ \quad (1)$$

where *SH* is an amphoteric solvent and can be pure water, an aqueous organic mixture, or a pure organic compound. Although the fictitious solvent species *SH* can be a mixture of compounds and thus composes of two types of molecules, it behaves as a single compound accepting and donating protons [5–7]. However, it is convenient to define the solute-free solvent mole fraction as:

$$x_S = \frac{\tilde{n}_S}{\tilde{n}_{Org} + \tilde{n}_W} \quad (2)$$

where *S* refers to either the organic compound (*Org*) or water (*W*) and $\tilde{n}_{Org}$ and $\tilde{n}_W$ are the total number of moles of the organic compound and water, respectively. The mean relative molar mass of the solute-free solvent mixture is:

$$M^*_{SH} = x_{Org}\tilde{M}_{Org} + x_W\tilde{M}_W \quad (3)$$

where $\tilde{M}_{Org}$ and $\tilde{M}_W$ are the respective molar masses of pure alcohol and water. The total mass of the solute-free solvent and the molality of an ionic solute species i (m° = 1 mol kg^{-1}) per 1 kg of solvent are:

$$\tilde{m}_{SH} = \tilde{m}_{Org} + \tilde{m}_W \quad (4)$$

$$m_i = \frac{\tilde{n}_i}{\tilde{m}_{SH}} \quad (5)$$

where $\tilde{m}_{Org}$ and $\tilde{m}_W$ are the total masses in kilograms of pure organic compound and water, respectively, and $\tilde{n}_i$ is the total number of moles of species *i*. For the ionic solute species, the asymmetric convention is applied. By use of the molality scale, the chemical potential of an ion *i* is:

$$\mu_i = \mu_i^\otimes + RTln\left(m_i\gamma_{i,m}\right) \quad (6)$$

where $\mu_i^\otimes$ is the standard state chemical potential of the ion *i* on the molality scale at *T*, *p*, and solvent composition x_s. $\gamma_{i,m}$ is the unsymmetric molality activity coefficient, where $\gamma_{i,m} \to 1$ as $\sum_i m_i \to 0$ at the solvent composition x_s. The standard state of the solvent mixture id defined at system *T*, *p* and x_s of the pure fictitious solvent SH.

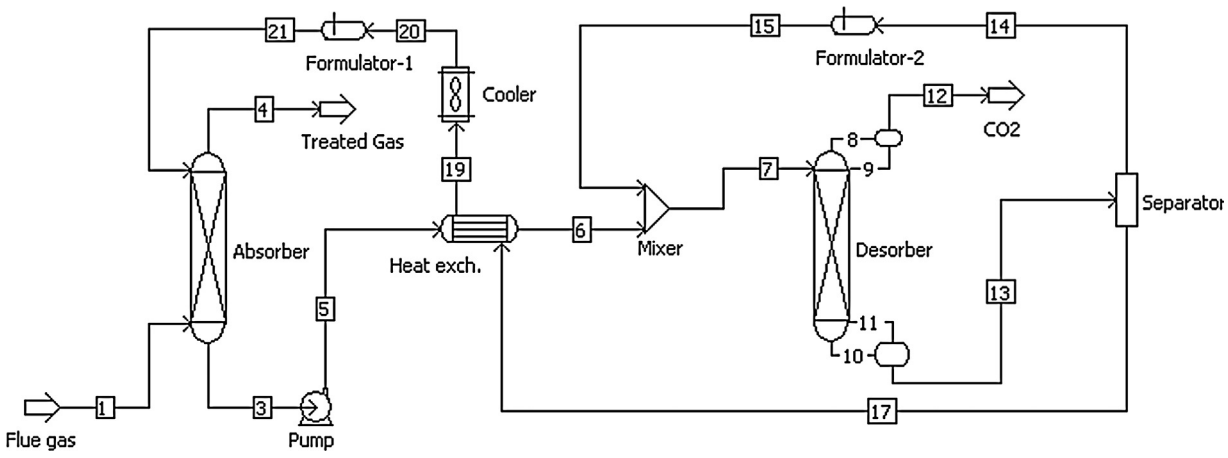

Fig. 1. Schematic flowsheet of process concept.

The apparent equilibrium constants of the alkanolamines in aqueous organic solvents can be determined by electromotive force (EMF) measurements using a combined glass pH electrode [2,3,8–11]. A two-cell system was used:

$$\mathrm{Ag(s), AgCl(s)} \mid \mathrm{3\ M\ KCl(aq)} \parallel \mathrm{HCl(aq}, \overline{m}_{HCl}) \parallel \mathrm{Glass\ Electrode} \quad \text{(I)}$$

and

$$\mathrm{Ag(s), AgCl(s)} \mid \mathrm{3MKCl(aq)} \parallel \mathrm{HCl}(x_{Org}, \overline{m}_{HCl})\ldots\mathrm{R} - \mathrm{NH_2}(x_{Org}, \overline{m}_{R-NH_2}) \parallel \mathrm{GlassElectrode} \quad \text{(II)}$$

where x_{Org} is the mole fraction of the alcohol defined by Eq. (2). The activity of a pure solid was set to unity, and the Nernst equation for cell (I) resulted in:

$$E_I = E^\circ(T_I) - \frac{RT_I}{F} \ln\left(a_{H_3O^+} a_{Cl^-}\right)_I \quad (7)$$

and for cell (II):

$$E_{II} = E^\circ(T_{II}) - \frac{RT_{II}}{F} \ln\left(a_{SH_2^+} a_{Cl^-}\right)_{II} \quad (8)$$

Both cells were kept at the same temperature, $T_I = T_{II}$, thus the standard potentials were equal, $E^\circ(T_I) = E^\circ(T_{II})$:

$$T_{II} \ln\left(a_{SH_2^+} a_{Cl^-}\right)_{II} = \frac{F(E_I - E_{II})}{R} + T_I \ln\left(a_{H_3O^+} a_{Cl^-}\right)_I \quad (9)$$

As HCl was assumed to be completely dissociated, the dissociation of water could be neglected in cell (I). The mole balances of the alkanolamine, HCl, and the solvent in cell (II) were:

$$\overline{n}_{R-NH_2} = n_{R-NH_2} + n_{R-NH_3^+} \quad (10)$$

$$\overline{n}_{HCl} = n_{Cl^-} \quad (11)$$

$$\overline{n}_{SH} = n_{SH} + n_{SH_2^+} + n_{S^-} \quad (12)$$

Electroneutrality resulted in:

$$n_{R-NH_3^+} + n_{SH_2^+} = n_{Cl^-} + n_{S^-} \quad (13)$$

The chemical equilibrium condition for the autoprotolysis of the solvent, K_{ap}, was:

$$K_{ap}(T, x_{Alc}) = \frac{a_{SH_2^+} a_{S^-}}{a_{SH}^2} \quad (14)$$

and the equilibrium condition for the dissociation of the protonated alkanolamine was:

$$K_a(T, x_{Alc}) = \frac{a_{R-NH_2} a_{SH_2^+}}{a_{R-NH_3^+} a_{SH}} \quad (15)$$

For a given temperature and composition, the electromotive forces E_I and E_{II} and the temperature in each cell were measured. The activities of HCl and KCl were estimated using the excess energy model of Pitzer from Holmes et al. [12] and Pabalan and Pitzer [13], respectively. A very brief outline of the excess energy model of Pitzer used in the present work is given in Appendix A. The activities of the ionic compounds present in cell II were approximated by the modified Debye–Hückel term in Pitzer's equation, i.e. neglecting binary and ternary interaction parameters [14]. The activity coefficient of the unprotonated alkanolamine was set to unity for all molalities, temperatures, and solvent compositions. The activity of the solvent mixture, *SH*, followed from the Gibbs–Duhem equation. The influence of the pressure on the chemical reactions was neglected, and set to 1 bara during aforementioned calculations. The changes in the compositions of the electrolyte cells due to the outflow of KCl electrolyte from the electrode were neglected. The autoprotolysis constant, $K_{ap}(T, x_{Alc})$, was taken from Fonrodona et al. [6]. In the absence of temperature dependent autoprotolysis constants [6,7] and autoprotolysis constants of sulfolane mixtures, only the values at 298.15 K for sulfolane was used [15]. With the given information Eqs. (9)–(15) were solved iteratively to yield the 'true' number of moles of each species present in cell II, as well as a preliminary value of the dissociation constant of the protonated alkanolamine in the aqueous organic solvent. This dissociation constant was called preliminary because it was calculated out of a set of equations in which for cell II the activities were not exactly known. The experiments were performed at different overall molalities of the alkanolamine, and the 'true' equilibrium constant of the dissociation of the protonated alkanolamine was determined in a two-step linear extrapolation procedure:

$$\lim_{\substack{x_{Org} = \text{const.} \\ \overline{m}_{HCl,II} = \text{const.} \\ \overline{m}_{R-NH_2} \to 0}} \left[K_{\mathrm{a,exptl}}\left(T, x_{Org}, \overline{m}_{HCl,II}, \overline{m}_{R-NH_2}\right)\right] = K_{\mathrm{a,exptl}}\left(T, x_{Org}, \overline{m}_{HCl,II}\right) \quad (16)$$

Table 1
Chemicals.

Chemical	CAS no.	Purity	Supplier
MEA	[141-43-5]	≥ 99%	Sigma–Aldrich
MDEA	[105-59-9]	≥ 99%	Sigma–Aldrich
t-Butanol	[75-65-0]	≥ 99.5%	Sigma–Aldrich
Methanol	[67-56-1]	≥99%	Sigma–Aldrich
Triethanolamine	[102-71-6]	99 %	Sigma–Aldrich
Sulfolane	[126-33-0]	99%	Sigma–Aldrich
HCl	[7647-01-0]	99%	Merck

Table 2
Dielectric constants, ϵ.

Chemical	ϵ	T/K	Ref.
MEA	32.6	298.15	[17]
MDEA	22.0	298.15	[17]
t-butanol	12.5	293.15	[18]
Methanol	32.6	298.15	[18]
Sulfolane	44.50	293.47	[19]
Triethanolamine	28.82	298.15	[20]
Water	78.3	298.15	[21]

Table 3
Experimental results of the dissociation constants of protonated MEA in *t*-butanol–water.

Run no.	T/K	x_{TBA}	$\ln(K_a)$	Avg. dev./%	Max. dev./%
1	283.02	0.20	−21.47	0.299	0.691
2	293.15	0.20	−20.87	0.151	0.325
3	298.15	0.20	−20.52	0.145	0.334
4	303.19	0.20	−20.05	0.167	0.393
5	313.11	0.20	−19.47	0.112	0.277
6	323.16	0.20	−18.73	0.098	0.228
7	333.17	0.20	−18.22	0.089	0.204
8	342.94	0.20	−17.56	0.082	0.198
9	352.99	0.20	−17.03	0.110	0.386
10	283.16	0.40	−20.59	0.550	1.774
11	293.16	0.40	−19.90	0.225	0.526
12	298.15	0.40	−19.48	0.136	0.349
13	303.14	0.40	−19.12	0.133	0.295
14	313.14	0.40	−18.32	0.129	0.307
15	323.15	0.40	−17.64	0.100	0.179
16	333.04	0.40	−17.04	0.115	0.309
17	343.42	0.40	−16.27	0.119	0.221
18	353.22	0.40	−15.63	0.138	0.281
19	283.10	0.60	−19.53	0.353	0.693
20	293.15	0.60	−18.93	0.083	0.130
21	298.19	0.60	−18.53	0.177	0.440
22	303.17	0.60	−18.01	0.255	0.616
23	313.26	0.60	−17.35	0.248	0.438
24	323.27	0.60	−16.46	0.105	0.209
25	333.38	0.60	−15.72	0.125	0.220
26	343.18	0.60	−14.98	0.260	0.471
27	353.33	0.60	−14.18	0.461	0.764
28	283.18	0.80	−17.84	0.201	0.365
29	293.15	0.80	−17.87	0.060	0.128
30	298.15	0.80	−17.49	0.070	0.118
31	303.20	0.80	−17.19	0.097	0.158
32	313.23	0.80	−16.41	0.131	0.236
33	323.11	0.80	−15.51	0.490	0.980
34	333.10	0.80	−14.58	0.080	0.160
35	343.49	0.80	−13.82	0.739	1.288
36	353.05	0.80	−13.36	0.061	0.091
38	293.23	0.95	−17.13	0.129	0.286
39	298.16	0.95	−17.07	0.922	1.785
40	303.19	0.95	−16.61	0.374	0.635
41	313.39	0.95	−15.37	0.273	0.695
42	323.31	0.95	−14.66	0.260	0.417
43	333.55	0.95	−13.42	0.296	0.366
44	343.32	0.95	−12.90	0.183	0.366
45	353.24	0.95	−11.12	0.483	1.019

$$\lim_{\substack{x_{Org}=\text{const.}\\ \overline{m}_{HCl,II}\to 0}} \left[K_{a,exptl}\left(T, x_{Org}, \overline{m}_{HCl,II}\right)\right] = K_a\left(T, x_{Org}\right) \quad (17)$$

However, since $\overline{m}_{HCl,II} \leq 0.01\,\text{mol kg}^{-1}$, the second extrapolation was not necessary.

3. Thermodynamic relations

To the experimentally determined dissociation constants, the well-known thermodynamic relations can be applied:

$$\Delta_r G_m = -RT \ln K_a \quad (18)$$

$$\Delta_r H_m = -R\frac{d\ln K_a}{d(1/T)} \quad (19)$$

and the change of standard state properties ($T = T^{\circ}$=298.15 K) for the dissociation of a protonated alkanolamine in aqueous organic solvents were calculated from Eqs. (18) and (19) by the use of [16]:

$$\ln K_a = \frac{A}{T} + B + C\ln(T) \quad (20)$$

Table 4
Experimental results of the dissociation constants of protonated MDEA in *t*-butanol–water.

Run no.	T/K	x_{TBA}	$\ln(K_a)$	Avg. dev./%	Max. dev./%
46	283.10	0.20	−19.30	0.300	0.499
47	293.21	0.20	−18.42	0.123	0.223
48	298.15	0.20	−18.03	0.272	0.620
49	303.10	0.20	−17.82	0.044	0.089
50	313.16	0.20	−17.38	0.154	0.201
51	323.21	0.20	−16.82	0.083	0.251
52	333.15	0.20	−16.34	0.304	0.149
53	343.11	0.20	−15.80	0.230	0.612
54	353.13	0.20	−15.26	0.366	0.656
55	283.11	0.40	−17.82	0.153	0.358
56	293.15	0.40	−17.30	0.072	0.167
57	298.15	0.40	−17.01	0.083	0.194
58	303.20	0.40	−16.77	0.136	0.268
59	313.16	0.40	−16.08	0.122	0.290
60	323.14	0.40	−15.47	0.148	0.300
61	333.19	0.40	−14.92	0.146	0.282
62	343.28	0.40	−14.22	0.383	0.704
63	353.27	0.40	−13.74	0.457	0.773
64	283.09	0.60	−16.92	0.573	1.023
65	293.15	0.60	−16.01	0.200	0.295
66	298.19	0.60	−15.83	0.171	0.412
67	303.21	0.60	−15.43	0.157	0.271
68	313.24	0.60	−14.81	0.215	0.443
69	323.26	0.60	−14.16	0.324	0.605
70	333.18	0.60	−13.44	0.325	0.691
71	343.32	0.60	−12.91	0.749	1.487
72	353.46	0.60	−12.58	1.070	0.628
73	283.13	0.80	−15.27	0.520	0.969
74	293.17	0.80	−14.79	0.336	0.833
75	298.11	0.80	−14.68	0.255	0.385
76	303.11	0.80	−14.40	0.068	0.101
77	313.23	0.80	−13.71	0.267	0.534
78	323.16	0.80	−12.81	0.303	0.603
79	333.09	0.80	−12.27	0.354	0.655
80	343.76	0.80	−11.47	0.462	0.663
81	353.50	0.80	−10.87	0.243	0.364
82	283.14	0.95	−13.70	0.807	1.613
83	293.15	0.95	−13.67	0.242	0.329
84	298.15	0.95	−13.45	0.192	0.314
85	303.10	0.95	−13.52	0.601	1.115
86	313.29	0.95	−12.21	0.335	0.669
87	323.20	0.95	−11.19	0.641	1.164
88	333.21	0.95	−10.24	0.626	1.252
89	343.58	0.95	−9.64	1.080	2.159
90	353.36	0.95	−8.37	0.911	1.819

Table 5
Experimental results of the dissociation constants of protonated MEA in sulfolane–water.

Run no.	T/K	$x_{Sulf.}$	$\ln(K_a)$	Avg. dev./%	Max. dev./%
91	283.15	0.20	−21.95	0.434	0.767
92	293.15	0.20	−21.40	0.213	0.510
93	298.15	0.20	−21.03	0.155	0.362
94	303.15	0.20	−20.59	0.224	0.524
95	313.35	0.20	−19.91	0.214	0.492
96	323.20	0.20	−19.24	0.226	0.534
97	333.27	0.20	−18.62	0.229	0.515
98	343.29	0.20	−17.97	0.170	0.273
99	353.18	0.20	−17.44	0.298	0.617
100	283.11	0.40	−21.17	0.463	1.093
101	293.15	0.40	−20.54	0.292	0.628
102	298.16	0.40	−20.34	0.195	0.356
103	303.21	0.40	−19.96	0.164	0.323
104	313.14	0.40	−19.27	0.163	0.343
105	323.21	0.40	−18.56	0.201	0.366
106	333.18	0.40	−17.93	0.184	0.326
107	343.23	0.40	−17.28	0.211	0.436
108	353.21	0.40	−16.73	0.253	0.577
109	283.10	0.60	−21.10	0.404	0.948
110	293.15	0.60	−20.38	0.160	0.328
111	298.15	0.60	−19.96	0.194	0.445
112	303.16	0.60	−19.59	0.197	0.453
113	313.11	0.60	−18.92	0.164	0.370
114	323.19	0.60	−18.23	0.182	0.375
115	333.18	0.60	−17.57	0.177	0.340
116	343.15	0.60	−16.92	0.304	0.777
117	353.32	0.60	−16.36	0.303	0.870
118	283.16	0.80	−21.01	0.333	0.795
119	293.15	0.80	−20.20	0.222	0.518
120	298.14	0.80	−19.79	0.203	0.488
121	303.15	0.80	−19.39	0.199	0.487
122	313.15	0.80	−18.66	0.200	0.466
123	323.24	0.80	−17.92	0.210	0.492
124	333.26	0.80	−17.21	0.357	0.821
125	343.37	0.80	−16.49	0.366	0.788
126	353.19	0.80	−15.98	0.392	0.837
127	283.14	0.95	−21.25	0.523	1.177
128	293.15	0.95	−20.36	0.498	1.063
129	298.15	0.95	−19.96	0.356	0.731
130	303.15	0.95	−19.56	0.283	0.539
131	313.19	0.95	−18.77	0.259	0.495
132	323.16	0.95	−18.01	0.237	0.450
133	333.30	0.95	−17.33	0.231	0.502
134	343.37	0.95	−16.59	0.232	0.625
135	353.26	0.95	−15.89	0.244	0.653

Table 6
Experimental results of the dissociation constants of protonated MDEA in sulfolane–water.

Run no.	T/K	$x_{Sulf.}$	$\ln(K_a)$	Avg. dev./%	Max. dev./%
136	283.15	0.20	−20.09	0.424	1.015
137	293.21	0.20	−19.22	0.259	0.464
138	298.15	0.20	−19.01	0.170	0.298
139	303.15	0.20	−18.70	0.213	0.462
140	313.18	0.20	−18.10	0.184	0.377
141	323.11	0.20	−17.58	0.188	0.389
142	333.24	0.20	−17.08	0.179	0.368
143	343.19	0.20	−16.61	0.184	0.387
144	353.15	0.20	−16.19	0.251	0.565
145	283.15	0.40	−19.02	0.485	0.892
146	293.15	0.40	−18.65	0.272	0.564
147	298.15	0.40	−18.45	0.307	0.494
148	303.15	0.40	−18.20	0.225	0.622
149	313.22	0.40	−17.60	0.230	0.616
150	323.21	0.40	−17.03	0.253	0.675
151	333.20	0.40	−16.50	0.261	0.670
152	343.33	0.40	−15.98	0.273	0.675
153	353.52	0.40	−15.46	0.384	0.904
154	283.11	0.61	−18.93	0.561	1.170
155	293.15	0.61	−18.33	0.398	0.871
156	298.10	0.61	−18.14	0.216	0.508
157	303.15	0.61	−17.88	0.134	0.269
158	313.15	0.61	−17.29	0.077	0.155
159	323.27	0.61	−16.71	0.131	0.291
160	333.25	0.61	−16.17	0.086	0.204
161	343.23	0.61	−15.65	0.141	0.351
162	353.54	0.61	−15.17	0.146	0.477
163	283.16	0.80	−18.82	0.666	1.373
164	293.15	0.80	−18.31	0.462	0.956
165	298.15	0.80	−17.87	0.321	0.730
166	303.20	0.80	−17.58	0.237	0.536
167	313.21	0.80	−16.97	0.177	0.396
168	323.26	0.80	−16.39	0.204	0.441
169	333.18	0.80	−15.87	0.156	0.342
170	343.31	0.80	−15.35	0.270	0.781
171	353.60	0.80	−14.90	0.300	1.050
172	283.16	0.95	−19.03	0.842	2.013
173	293.15	0.95	−18.65	0.652	1.447
174	298.15	0.95	−18.43	0.405	0.751
175	303.15	0.95	−17.87	0.270	0.614
176	313.21	0.95	−17.29	0.205	0.293
177	323.27	0.95	−16.70	0.234	0.603
178	333.22	0.95	−16.14	0.296	0.764
179	343.59	0.95	−15.61	0.487	0.661
180	353.59	0.95	−15.04	0.356	0.805

4. Experimental

The experimental setup was similar to the one described by Hamborg et al. [2,3,8]. Measurements were conducted at 10 K intervals from (283 to 353) K and at 298 K. The overall molalities of HCl in cell (I) and cell (II) were held constant ($\overline{m}_{HCl,I} = \overline{m}_{HCl,II} \approx 0.01$ mol kg^{-1}). The molalities of the alkanolamines were varied between (0.0187 and 0.1066) mol kg^{-1}. Measurements where the temperature in cell (I) and in cell (II) deviated by more than ±0.1 K were not considered in the aforementioned calculations.

5. Chemicals

Chemicals used for experiments are listed below in Table 1 and were used as supplied. HCl was provided as 0.1 M standard solutions, and was diluted to the desired molality by weight. The demineralized water and the alcohols were purified by individual vacuum distillation, and the alcohol–water solvents were prepared by weight. The values of dielectric constants are included in Table 2.

6. Results and discussion

Experimental results at averaged temperatures for the dissociation constants of protonated MEA, MDEA in t-butanol–water, sulfolane–water and TEA in methanol–water are given in Table 3–7. The experimental uncertainties are ±0.04 $\ln(K_a)$ units due to inaccuracies in E_I and E_{II} of ±0.5 mV. The results are also given with the average and maximum relative deviation between the experimental data and the values of the linear fit from Eqs. (16) and (17). These numbers provide insight into the accuracy of the linear extrapolation. The EMF measurement data are tabulated and provided as electronic Supplementary Material with corresponding 'Run no.'. Run no. 37 was not carried out due to the solubility limitations of t-butanol in water.

A decreased basic strength of the protonated alkanolamines with increased fractions of the organic compound and temperature can be clearly observed in the results presented in Tables 3–7. The largest effect is observed for t-butanol–water mixtures as solvents. This is as expected since t-butanol–water solvents has the lowest values of the dielectric constants compared to sulfolane–water and methanol–water solvents.

Table 7
Experimental results of the dissociation constants of protonated TEA in methanol–water.

Run no.	T/K	$x_{MeOH.}$	ln(K_a)	Avg. dev./%	Max. dev./%
181	283.10	0.20	−18.10	0.071	0.250
182	293.07	0.20	−17.66	0.075	0.154
183	298.16	0.20	−17.35	0.088	0.293
184	303.14	0.20	−17.11	0.027	0.068
185	313.14	0.20	−16.62	0.067	0.125
186	323.14	0.20	−16.16	0.080	0.144
187	283.11	0.40	−17.81	0.102	0.166
188	293.24	0.40	−17.24	0.064	0.116
189	298.25	0.40	−16.95	0.048	0.112
190	303.16	0.40	−16.67	0.060	0.124
191	313.15	0.40	−16.13	0.189	0.412
192	323.15	0.40	−15.65	0.218	0.580
193	283.25	0.60	−17.22	0.353	0.614
194	293.25	0.60	−16.56	0.094	0.021
195	298.05	0.60	−16.43	0.207	0.355
196	303.25	0.60	−16.11	0.167	0.346
197	313.15	0.60	−15.72	0.162	0.356
198	323.05	0.60	−15.04	0.251	0.460
199	283.15	0.80	−16.68	0.661	1.071
200	293.15	0.80	−16.10	0.280	0.684
201	298.05	0.80	−15.71	0.263	0.391
202	303.05	0.80	−15.53	0.132	0.217
203	313.25	0.80	−14.96	0.166	0.357
204	323.35	0.80	−14.47	0.142	0.322
205	283.27	0.95	−16.41	0.236	0.593
206	293.25	0.95	−15.66	0.300	0.584
207	298.27	0.95	−15.61	0.260	0.664
208	303.15	0.95	−15.26	0.313	0.496
209	313.17	0.95	−14.75	0.239	0.421
210	323.35	0.95	−14.16	0.100	0.288

The values of $\Delta_r G^0_m$ and $\Delta_r H^0_m$ given in Table 8 can be calculated from Eqs. (18) and (19). The values of $\Delta_r G^0_m$, or pK_a, represent the basic strength of the compounds and the values of $\Delta_r H^0_m$ indicate the change in the basic strength of the compound.

From the results it can be concluded that;

(1) solvents with lower dielectric constants, lower the dissociation of the unprotonated alkanolamine and thus the basic strength of the alkanolamines. From a Bronsted plot [22,23], a higher basic strength of the protonated alkanolamine can indicate a higher reaction rate of the alkanolamine with an acid gas (e.g. CO_2), although, for accurate determination of reaction rate constants, separate kinetic measurements have to be considered.

(2) the acid gas reacts with the solvent in a basic environment in the absorber section and released in the desorber section in an acid gas plant. The temperature swing between the absorber and desorber section ranges from 313 to 393 K. [1] During this cooling/heating cycle of the solvent, it changes its basic strength in order to absorb or desorb the acid gas. A higher value of $\Delta_r H^0_m$, e.g. a higher temperature dependent change of the dissociation constant, results in a favorable shift of the basic strength of the alkanolamine during the cooling/heating cycle of the absorber/desorber sections.

7. Conclusion

The dissociation constants of protonated monoethanolamine, N-methyldiethanolamine and triethanolamine have been determined in *t*-butanol–water, methanol–water and sulfolane–water solvents. The mole fractions or the organic compounds were ranging from 0.2 to 0.95 and the temperatures from 283 to 353 K. At 298.15 K standard state thermodynamic properties can be derived from the results. The basic strength of the protonated alkanolamine decreases with decreasing dielectric constant and increasing temperature of the solvent.

The results provide information about the CO_2 removal performance given by the temperature dependence on the dissociation constants of these solutions, and can be further used in the interpretation of kinetic rate parameter measurements and modeling of CO_2 removal and for acid gas treating processes.

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Table 8
Values of the standard state thermodynamic properties ($T = T^\circ$=298.15 K) of MEA, MDEA and TEA in aqueous organic solvents.

x_{Alc}	$\Delta_r G^\circ_m$ (kJ mol^{-1})	pK_a	$\Delta_r H^\circ_m$ (kJ mol^{-1})	$\Delta_r G^\circ_m$ (kJ mol^{-1})	pK_a	$\Delta_r H^\circ_m$ (kJ mol^{-1})
	MEA in water			MDEA in water		
0.00	53.90	9.44	48.6	48.87	8.56	34.9
	TEA in water					
0.00	44.07	7.72	31.3			
	MEA in *t*-butanol–water			MDEA in *t*-butanol–water		
0.20	49.70	8.91	44.76	45.08	7.83	45.7
0.40	48.20	8.46	55.2	42.12	7.39	43.1
0.60	45.78	8.05	56.1	39.07	6.87	53.1
0.80	42.79	7.60	44.6	36.10	6.37	41.8
0.95	41.88	7.41	56.4	34.21	6.07	66.3
	MEA in sulfolane–water			MDEA in sulfolane–water		
0.20	51.96	9.13	51.4	47.09	8.26	47.6
0.40	50.18	8.83	48.0	45.57	8.08	36.2
0.60	49.51	8.65	54.3	44.87	7.88	40.8
0.80	49.05	8.59	58.7	44.34	7.76	46.6
0.95	49.49	8.67	60.3	45.22	8.02	44.3
	TEA in methanol–water [a]					
0.20	43.05	7.53	36.5			
0.40	42.02	7.36	41.0			
0.60	40.65	7.14	38.8			
0.80	39.09	6.82	42.2			
0.95	38.50	6.78	40.8			

[a] Values given at the measured experimental temperature.

Appendix A. Outline of the model of Pitzer

A very brief outline of the model of Pitzer introduced by Pitzer [24] is given below. For an electrolyte solution containing $\tilde{m}_{SH}$ kilograms of solvent, with molalities m_i, m_j,. . ., of solute spices $i, j, \ldots$, Pitzer [24] introduced the equation for the excess Gibbs energy:

$$\frac{G^{ex}}{RT\tilde{m}_{SH}} = f(I_m) + \sum_i \sum_j m_i m_j B_{ij} + \sum_i \sum_j \sum_k m_i m_j m_k C_{ijk} + \ldots \tag{A.1}$$

Pitzer [24] further derived the expression for the activity coefficient. For the dissolved species $i:j$, the activity coefficients were estimated by:

$$ln\left(\gamma_{ij,m}\right) = -A_\phi \left[\frac{\sqrt{I_m}}{1+b\sqrt{I_m}} + \frac{2}{b} ln\left(1+b\sqrt{I_m}\right)\right] + mB_{ij} + 3m^2 C_{ij} \tag{A.2}$$

where I_m is defined as:

$$I_m = \frac{1}{2}\sum_{q=i,j} m_q z_q^2 \tag{A.3}$$

and $b = 1.2\ \mathrm{kg}^{1/2}\ \mathrm{mol}^{-1/2}$. The Debye–Hückel term was given as:

$$A_\phi = \frac{1}{3}\sqrt{2\pi N_A \rho}\left(\frac{e^2}{4\pi\epsilon_0\epsilon_{SH}kT}\right)^{1.5} \tag{A.4}$$

where the specific density, ρ, and the relative dielectric constant, ϵ_{SH}, of the (solute-free) solvent mixture, as well as the parameter b given above, are solvent composition dependent parameters. ρ was taken from Saul and Wagner [25], Kipkemboi and Easteal [26], and Sacco et al. [27] for water, the *t*-butanol–water solvent, and the sulfolane–water solvent respectively. ϵ, was taken from Bradley and Pitzer [28], Akerlöf [18] and Klein et al. [29] for water, the *t*-butanol–water and sulfolane–water solvents. The parameter b was set to $1.2\ \mathrm{kg}^{1/2}\ \mathrm{mol}^{-1/2}$ for aqueous solutions by Pitzer [24], and this value was assumed to be independent of the solvent composition and the value for pure water was applied. [30] The second virial coefficient is given:

$$B_{ij} = 2\beta_{ij}^{(0)} + \left(\frac{2\beta_{ij}^{(1)}}{\alpha^2 I_m}\right)\left[1 - \left(1 + \alpha I_m^{1/2} - \frac{\alpha^2 I_m}{2}\right) exp\left(-\alpha I_m^{1/2}\right)\right] \tag{A.5}$$

where $\beta_{ij}^{(0)}$, $\beta_{ij}^{(1)}$ and C_{ij} are salt specific interaction parameters. For the case considered here, $\alpha = 2.0\ \mathrm{kg}^{1/2}\ \mathrm{mol}^{-1/2}$. The activity of the solvent mixture followed from the Gibbs–Duhem equation in the form of:

$$ln(a_{SH}) = \frac{M_{SH}^*}{1000}\left\{2A_\phi \frac{I_m^{1.5}}{1+b\sqrt{I_m}} - \sum_{i\neq SH} m_i\right\} \tag{A.6}$$

where M_{SH}^* was the molecular weight of the solvent mixture.

A.1. Interaction parameters for KCl in the model of Pitzer

The following section reports the temperature dependence of the ion interaction parameters for KCl given by Pabalan and Pitzer [13]. The interaction parameters are calculated from Eq. (A.7) and Table A.9. T is the temperature in Kelvin, T_R is 298.15 K, P is the pressure in bar and P_R is 179 bar. The density of water, ρ_W, was taken from Saul & Wagner [25]. The pressure, P, was set to 1 bar.

Table A.9
Parameters for Eq. (A.7).

parameter	$\beta_{KCl}^{(0)}$ (kg mol^{-1})	$\beta_{KCl}^{(1)}$ (kg mol^{-1})	C_{KCl} (kg^2 mol^{-2})
u_1	-2.10289×10^{-2}	2.20813×10^{-1}	0.0
u_2	6.03967×10^{-1}	-4.61849	7.64891×10^{-4}
u_3	3.67768×10^{-3}	-4.10116×10^{-2}	0.0
u_4	-7.05537×10^{-6}	1.10445×10^{-4}	-1.12131×10^{-8}
u_5	1.97968×10^{-9}	-4.73196×10^{-8}	1.72256×10^{-11}
u_6	-2.47588×10^{-3}	-2.74120×10^{-2}	0.0
u_7	1.44160×10^{-1}	3.32883×10^{-1}	-5.71188×10^{-3}
$f_L(T_r, 1\ \mathrm{bar})$	6.77136×10^{-4}	9.67854×10^{-4}	-4.12364×10^{-5}
$f_L(T_r, P_r)$	6.56838×10^{-4}	9.67854×10^{-4}	-4.12364×10^{-5}
$f_G(T_r, 1\ \mathrm{bar})$	4.8080×10^{-2}	2.18752×10^{-1}	-3.94×10^{-4}
$f_G(T_r, P_r)$	5.0038×10^{-2}	2.18752×10^{-1}	-3.94×10^{-4}
K_1	-2931.268116	6353.355434	28.172180
K_2	-33.953143	193.004059	-0.125567

Table A.10
Parameters for Eq. (A.9).

parameter	B_{KCl}^V (kg mol^{-1} bar^{-1})
q_1	0.0
q_2	0.0
q_3	9.45015×10^{-8}
q_4	-2.90741×10^{-10}
q_5	3.26205×10^{-3}
q_6	8.39662×10^{-7}
q_7	0.0
q_8	-4.41638×10^{-9}
q_9	6.71235×10^{-12}
q_{10}	-4.42327×10^{-5}
q_{11}	-7.97437×10^{-10}
q_{12}	0.0
q_{13}	4.12771×10^{-12}
q_{14}	-6.24996×10^{-15}
q_{15}	4.16221×10^{-8}

The pressure dependence of the thermodynamic properties were calculated from Eq. (A.8) and Table A.10. A complete description of the equations below are given by Pabalan and Pitzer [13].

$$\begin{aligned} f(T,P_r) = {} & \frac{u_1T^2}{6} + \frac{u_2T}{2} + \frac{u_3T^2(ln(T)/2 - 5/12)}{3} + \frac{u_4T^3}{12} \\ & + \frac{u_5T^4}{20} + u_6\left[\frac{T}{2} + \frac{3(227)^2}{2T} + \frac{227\,(T-227)\,ln\,(T-227)}{T}\right] \\ & - u_7\left[\frac{2\,(647-T)\,ln\,(647-T)}{T} + ln\,(647-T)\right] - \frac{K_1}{T} \\ & - f_L(T_r,P_r)\left(\frac{T_r^2}{T}\right) + K_2 + f_G(T_r,P_R) \end{aligned} \tag{A.7}$$

$$\begin{aligned} & ln\gamma_\pm(P_2) - ln\gamma_\pm(P_1) \\ & = -\left[A_\phi(P_2) - A_\phi(P_1)\right]\left(\frac{I_m^{1/2}}{1+bI_m^{1/2}} + \frac{2}{b}ln\left(1+bI_m^{1/2}\right)\right) \\ & \quad + \int_{P_1}^{P_2}\left\{2m\left(\frac{\partial\beta_{ij}^{(0)}}{\partial P}\right)_T + \frac{2m}{\alpha^2 I_m}\left(\frac{\partial\beta_{ij}^{(1)}}{\partial P}\right)_T\right. \\ & \quad \left.\times\left[1-\left(1+\alpha I_m^{1/2} - \frac{\alpha^2 I_m}{2}\right)exp\left(-\alpha I_m^{1/2}\right)\right] + 3m^2\left(\frac{\partial C_{ij}}{\partial P}\right)_T\right\} dP \end{aligned} \tag{A.8}$$

Table A.11
Parameters for Eq. (A.11).

Parameter	$\beta^{(0)}_{HCl}$ (kg mol^{-1})	$\beta^{(1)}_{HCl}$ (kg mol^{-1})	C_{HCl} (kg^2 mol^{-2})
q_1	0.17690	0.2973	0.362×10^{-3}
q_2	−0.09140	16.147	0.0
q_3	0.0	-17.631×10^{-3}	0.0
q_4	-4.034×10^{-4}	0.0	-3.036×10^{-5}
q_5	0.620×10^{-4}	7.20×10^{-4}	0.0

where $\left(\partial\beta^{(0)}_{ij}/\partial P\right)_T = B^V_{ij}$ and B^V_{ij} is calculated from Eq. (A.9) and Table A.10. Further, in this case, $\left(\partial\beta^{(1)}_{ij}/\partial P\right)_T = 0$ and $\left(\partial C_{ij}/\partial P\right)_T = 0$.

$$f_V(T,P) = q_1 + \frac{q_2}{T} + q_3 T + q_4 T^2 + \frac{q_5}{647 - T} + P\left[q_6 + \frac{q_7}{T} + q_8 T + q_9 T^2 + \frac{q_{10}}{(647 - T)}\right] + P^2\left[q_{11} + \frac{q_{12}}{T} + q_{13} T + q_{14} T^2 + \frac{q_{15}}{(647 - T)}\right] \quad \text{(A.9)}$$

A.2. Interaction parameters for HCl in the model of Pitzer

The following section reports the density, pressure, and temperature dependence on the ion interaction parameters for HCl given by Holmes et al. [12]. The ion interaction parameters are given by Eq. (A.11) and Table A.11. T is the temperature in Kelvin, T^* is 1 K, P^* is 1 MPa and ρ^* is 1 kg m^{-3}. T_R, P_R and ρ_R are the reference temperature, pressure and density and are set to 298.15 K, 0.101325 MPa and 997.062 kg m^{-3}, respectively. The pressure and density, P and ρ, were set equal to the reference pressure and reference density. For HCl, the interaction parameter, C in Eq. (A.2), is defined:

$$C = \frac{1}{2} C_{HCl} \quad \text{(A.10)}$$

$$f(\rho, P, T) = q_1 + q_2 ln\left(\frac{\rho}{\rho_R}\right) + q_3\frac{(\rho - \rho_R)}{\rho^*} + q_4\frac{(T - T_R)}{T^*} + q_5\frac{(P - P_R)}{P^*} \quad \text{(A.11)}$$

Appendix B. Supplementary Data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.fluid.2013.08.040.

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